Preface

The field of strongly correlated organic conjugated molecules has witnessed immense activity in the last few decades, because of recent interest in device applications, using these materials. This has brought out a large number of interesting features, concerning their electronic structures. In this thesis, we address various issues concerning the electronic properties of large conjugated molecules. The objective of our research is to characterize different excitations in these systems by studying various ground and excited state properties like transition dipole moments, charge densities, permanent dipole moments and non-linear optical properties such as two photon absorption cross section and non-linear polarizabilities of different order. These properties of organic materials are widely exploited in fabricating various opto-electronic devices for up-converted lasing, optical power limiting, photo-dynamic therapy and three dimensional micro-fabrication. To compute these properties, we have employed various many-body techniques like configuration interaction (CI) technique, density matrix renormalization group (DMRG) method, time dependent many-body calculations, density functional theory (DFT) and semi-empirical methods. This thesis consists of seven chapters. In the following, we give a brief outline of the various chapters in this thesis.

The first chapter of this thesis provides an introduction to various classes of organic conjugated molecules, which include organic amines, donor-acceptor-donor systems, dendrimeric molecules and organic conjugated polymers. These materials possess high hole mobility, large quadratic non-linear response and low band gaps, which are exploited in various opto-electronic devices namely, organic light emitting diodes (OLEDS), organic photo-voltaic cells (OPV), organic field effect transistors (OFET) etc. This is followed by a brief description of various photo-physical processes, which includes single and bimolecular luminescence processes and multi-photon processes. In addition, we describe the underlying principles of electroluminescence (EL) phenomenon by a simple two-level diagram encompassing the molecular HOMO and LUMO levels. Finally we conclude this chapter by describing the underlying principles of most notable organic electronic devices like OLEDs, OPVs and OFETs.

The second chapter of this thesis provides an introduction to various many-body techniques, which are employed in studying different ground and excited state properties of the organic conjugated systems. Here, we first introduce the Schrödinger equation and the total molecular Hamiltonian, containing both the electronic and nuclear degrees of freedom. Since, we are mostly interested in the ground and low-lying electronic states of the molecular systems, we work within the Born-Oppenheimer approximation, where the electronic and nuclear degrees of freedom can be decoupled and can be solved independently. The resulting many-electron Hamiltonian can be further simplified by using an independent particle approximation. In this section, we also describe the Hartree-Fock (HF) theory, where the electron-electron interactions are included in a mean-field manner. The next section gives an overview of the DFT method, which include various exchange and correlation energy functional, used to obtain accurate ground state properties for organic conjugated molecules. The following two sections are devoted to the full CI method and a brief introduction to the

2^{nd} quantized notation of one and two-body operators, as discussed in subsequent chapters. Subsequently, we focus our attention on various Quantum cell models.

After noticing some of the major failures of the Hückel model, which completely neglects the electron-electron repulsion, we describe the Pariser-Parr-Pople (PPP) model, which takes into account the electron repulsion at a phenomenological level, under the "zero differential overlap" (ZDO) and the "σ-π separability" approximations. The next section gives a brief account of various semi-empirical model Hamiltonians like complete neglect of differential overlap (CNDO), intermediate neglect of differential overlap (INDO) and neglect of diatomic differential overlap (NDDO). The INDO scheme goes beyond CNDO and is used in subsequent chapters to obtain ground and excited state properties of organic conjugated molecules. Next, we move on to the methods for studying these model Hamiltonians. Here, we describe the construction of Diagrammatic Valence Bond (DVB) basis, which is used to study systems with less than or equal to 16 orbitals. Since, the size of the Hilbert space for such a Hamiltonian is often more than a million, the usual diagonalization procedure fails. Rettrup's algorithm provides a convenient way of obtaining few low-lying eigenvalues and eigenvectors of the FCI Hamiltonian. The eigenvectors are used to compute various properties like transition dipole moments, permanent dipole moments and correlation functions.

Since the FCI method is only applicable to small systems, we resort to various approximate methods like restricted configuration interaction (single configuration interaction and single and double configuration interaction) and density matrix renormalization group (DMRG) method. The restricted configuration interaction schemes are best suited to obtain ground and excited state energies and properties for weakly interacting systems. On the other hand, the DMRG method is best suited for quasi linear interacting systems. It is currently the best suited method for studying one and quasi-one dimensional systems.

The third chapter of the thesis deals with a time evolution study, which ascertain the role of the triplet state in the green emission peak of the ethyl-hexyl substituted polyfluorene (PF2/6) films. The blue emission of PF2/6 films is accompanied by a low energy green emission peak, around 500 nm in inert atmosphere. The intensity of this 500 nm peak is large in EL, compared to photoluminescence (PL) measurements. Furthermore, the green emission intensity reduces dramatically in presence of molecular oxygen. To understand this, we have modeled various non-radiative processes by time dependent quantum many body methods. These are (i) inter-system crossing (ISC) to study conversion of excited singlets to triplets, (ii) electron-hole recombination (e-hR) process in presence or absence of a paramagnetic impurity and (iii) quenching of excited triplet states in presence of oxygen molecules or metal ion impurities. We have employed the PPP Hamiltonian to model the molecules and have invoked electron-electron repulsions beyond ZDO approximation, while treating interactions between the organic molecule and the rest of the system. Our time evolution methods show that there is a large cross section for triplet formation in the e-hR process in the presence of paramagnetic impurity with degenerate orbitals. The triplet yield through e-hR process far exceeds that in the inter-system crossing pathway, clearly pointing to the large intensity of the 500 nm peak in EL compared to PL measurements. We have also modeled the triplet quenching process by a paramagnetic oxygen, which

shows a sizable quenching cross section especially for systems with large sizes. These studies show that the most probable origin of the experimentally observed low energy EL emission is the triplets.

In chapter four, we describe the origin of the unusual EL in tri-p-tolylamine based hole conductors. The PL and EL of thin films of TAPC (1,1-bis((di-4-tolylamino) phenyl) cyclo-hexane) are remarkably different. Instead, similar PL and EL is observed in films of the closely related donors like TTA (tri-p-tolylamine) and TPD (N,N′-diphenyl-N,N′-bis(3-methylphenyl)- [1,1′-biphenyl]-4,4′-diamine). Such films show a wide range of hole transport that depends on the morphology and on external parameters such as temperature and electric field. Restricted configuration interaction calculations performed on TTA, TAPC, TPD and radical ions of TTA, indicate that the unusual EL of TAPC films is due to direct recombination from a low-lying charge transfer (CT) state. The CT state is strongly stabilized compared to the transport gap by electrostatic interactions, which is related to disordered dipoles and charge-dipole interactions. The charge distributions of TTA^{+} and TTA^{-} indicate charge localization in the anion, that rationalizes low electron mobility as well as a strong charge-induced-dipole stabilization of the CT state. Our theoretical calculation assigns the EL as a consequence of direct emission from ion-pairs in films, following the exciplex route.

In chapter five, we turn our attention to the calculation of ground and excited state properties of donor-acceptor systems using the ab-initio DFT and INDO/S methods. The π-electron density in these chromophores are highly polarized, due to the presence of both electron donating (donor) and electron withdrawing (acceptor) group. In this chapter we focus on a special class of dipolar systems which is composed of a central malononitrile acceptor group, flanged by two donor substituents (thiophene rings). Such systems are commonly referred to as donor-acceptor-donor (D-A-D) systems. It is experimentally observed from fluorescence and cyclic-voltammetry experiments that by increasing the number of thiophene units in these molecules, the band gap shifts towards the red region and finally saturates around 2.0 eV. Density functional calculations along with INDO/SCI calculations corroborate this experimental finding. We also observe a strong intramolecular charge transfer phenomenon between the thiophene donor and the benzopyran acceptor, in this class of D-A-D systems. The charge transfer character increases with the increase of the thiophene units and finally saturates in the molecule containing 12 thiophene units, in conjugation with the benzopyran acceptor. Calculation of excited state properties like permanent dipole moments and the oscillator strengths are done using ZINDO-SCI method. We have also calculated the Stoke's shift and effect of solvents on the excited state energies for these class of compounds. All our theoretical results corroborates reasonably well with experiments.

In chapter six, we focus on studying linear and non-linear optical properties of dendrimers, using the DMRG method. We have used this method to study the linear and non-linear optical responses of first generation nitrogen based dendrimers with donor and acceptor groups. We have employed PPP Hamiltonian to model the interacting π-electrons in these systems. Within the DMRG method, we have used an innovative scheme to target excited states with large transition dipole to the ground state. This method reproduces optical gaps and polarization in small systems, where exact diag-

onalization of Hamiltonian is possible. We have used correction vector method, which tacitly takes into account the contribution of all excited states, to obtain the ground state polarizabilities, first hyperpolarizabilities and two photon absorption cross sections. In these dendrimeric systems we observed that the lowest optical excitations and the lowest triplet states are localized. It is interesting to note that the first hyperpolarizability saturates more rapidly with system size compared to linear polarizability, unlike linear polyenes.

Chapter seven deals with non-linear optical (NLO) properties of a class of weak donor-acceptor complexes. These weakly associated complexes are formed when the methyl substituted phenylenes (donors) are added to strong acceptors like chloranil (CHL) and di-chloro-di-cyano benzquinone (DDQ) in chloroform or in di-chloro methane solvent. The formation of such complexes is supported by the presence of a broad absorption maximum in the visible range of the spectrum, where neither the donor nor the acceptor absorbs. These complexes show strong charge-transfer (CT) interactions upon excitation, which result in strong NLO responses. By measuring the second harmonic signal and the depolarization ratios, using linear and circularly polarized light, the off-diagonal components of the first hyperpolarizability (β) tensor have been estimated. We have employed the SDCI method to estimate the β tensor, which is used in computing the macroscopic depolarization ratios. Our theoretical results compare well with experimental findings. By comparing the theoretically computed NLO properties with experimental results, we conclude that the most probable geometry of these complexes in solution is the parallel displaced configuration.